(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 417 700 A2**

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: 90117402.9

(51) Int. Cl.[5]: G01N 21/35, G01N 21/55

(22) Date of filing: 10.09.90

(30) Priority: 12.09.89 IL 91614

(43) Date of publication of application:
20.03.91 Bulletin 91/12

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB IT LI LU NL SE

(71) Applicant: THE STATE of ISRAEL Atomic Energy Commission Soreq Nuclear Research Center
Nahal Soreq
Yavne 70 600(IL)

(72) Inventor: Bornstein, Aharon
1, Marvad Haksamim Strasse
Holon 58845(IL)
Inventor: Wolfman, Dan
13, Brodetzky Strasse
Tel Aviv 69051(IL)
Inventor: Katz, Mordechai
46, Kaplinsky Strasse
Givatayim 53606(IL)

(74) Representative: Patentanwälte Grünecker, Kinkeldey, Stockmair & Partner
Maximilianstrasse 58
W-8000 München 22(DE)

(54) **Improvement in attenuated total reflection spectroscopy.**

(57) Method of ATR spectroscopy and substrate probe for use therein. The probe comprises a single optical fibre sensor, a bundle of such sensors, the sensing zone of each sensor being a small diameter cylindrical portion merging at least on the side of the light intake end into a frustoconical portion whose large diameter base is turned away from said small diameter cylindrical portion.

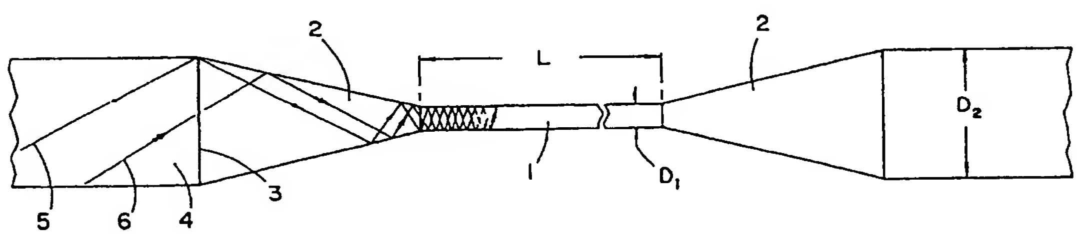

Fig. 1

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IMPROVEMENT IN ATTENUATED TOTAL REFLECTION SPECTROSCOPY

FIELD OF THE INVENTION

The present invention is in the field of optical spectroscopy. More specifically it relates to analytical spectroscopy based on the measurement by the so-called attenuated total reflection method which is based on the attenuation of evanescent waves propagating at the interface between an uncladded optical waveguide and a surrounding medium having a lower refraction index.

BACKGROUND OF THE INVENTION AND PRIOR ART

The following prior art description outlines the background of the invention mainly in relation to infrared (IR) spectroscopy, it being understood that the present invention is also applicable in spectroscopy employing light in other ranges such as ultraviolet and visible light.

Spectroscopy is widely used nowadays in qualitative and quantitative analysis of materials. Often infrared detection techniques are advantageous over spectroscopic techniques using radiation of shorter wavelengths, such as visible light, since organic and biological materials have characteristic sharp and relatively narrow absorption peaks in the IR region.

In the performance of a direct IR spectroscopic analysis a light beam is passed across a sample material, and the transmission is measured as function of wavelength which yields a characteristic spectrum. The measurements may be direct and yield an absorption spectrum or indirect and yield an emission spectrum.

The term "measurement" as used herein applies generally and indiscriminantly to detection, identification and quantitative measurement.

Common IR spectroscopic techniques suffer from an intrinsic problem which is due to the strong absorption of IR radiation. Because of this the substrate materials have, as a rule, to be diluted by a medium that is transparent in the infrared, e.g. a liquid such as Nujol (Trade Name) or a solid salt such as KBr. The ensuing high dilution of the sample may give rise to inaccuracies in the results.

An alternative method of direct spectroscopic measurement is the so-called Attenuated Total Reflection (ATR) method. This technique of recording the optical spectrum of a sample material uses an uncladded waveguide for the determination of the concentration of a test species dispersed in a liquid, solid or gaseous medium having a lower refractive index than the waveguide. It is based on total internal light reflection producing an evanescent light wave propagating along the waveguide/test medium interface and it measures the modulation of the evanescent light wave. The ATR technique enables to obtain accurate spectroscopic measurements with smaller amounts of sample materials than in common SR spectroscopy.

Analytical spectroscopic methods employing ATR are described, for example, in U.S. patents 4,447,546 and 4,558,014 and in WO 83/01112. These publications describe fluorimetric measurements made by total reflection fluorescence techniques.

The depth of penetration of the evanescent wave into the substrate medium is strongly dependent on the incidence angle of the internally reflected light, and the closer this angle is to the critical angle (beyond which there is no total reflection), the depth of penetration increases exponentially.

The intensity of the interaction between the light travelling inside the uncladded waveguide and the medium surrounding it, is dependent on the concentration of the solution; the intensity of absorption; the depth of penetration (which itself is dependent on the incidence angle of the internally reflected light); and the number of the internal light reflections per unit length which in turn is inversely proportional to the diameter of the fibre. An increase in the number of the internal reflections amplifies linearly the interaction of the light with the surrounding substrate whereas an increase of the incidence angle amplifies the interaction exponentially.

OBJECTS OF THE INVENTION

In the following, a measuring device comprising a vessel for holding a test fluid and fitted with a sensor will be referred to as "probe".

It is an object of the present invention to increase the sensitivity of spectroscopic measurements by the ATR method by intensifying the interaction between the waveguide and the surrounding test medium.

It is a further object of the invention to provide a probe with a highly sensitive optical sensor for use in the ATR method, suitable for measurements of small amounts of test materials, e.g. individual small droplets of the kind present in aerosols.

It is a still further object of the invention to provide means for direct spectroscopic measurement without need for any sensitizer reagents to

mediate between the sensor and the test medium.

It is also an object of the present invention to provide a so-called dynamic probe, i.e. an effective and highly sensitive probe adapted for the continuous monitoring of a through-flowing test fluid.

It is yet another object of the present invention to provide a disposable sensitive probe for use in the ATR method, suitable for sampling a test medium, for performing an ATR analysis and, if desired, for storing the sample as reference for future measurements.

These and other objects of the invention will become apparent from the following description.

SUMMARY OF THE INVENTION

In accordance with the present invention there is provided a method of performing a spectroscopic measurement by the attenuated total reflection (ATR) technique employing a tubular probe adapted to hold a substrate medium and fitted within with at least one optical fibre sensor having an unclad sensing zone and a light intake and emitting ends, characterised in that the sensing zone of each sensor is a small diameter cylindrical portion merging at least on the side of the light intake end into a frustoconical portion whose large diameter base is turned away from said small diameter cylindrical portion.

Preferably the small diameter cylindrical portion of the sensing zone of each sensor in a probe used in the performance of the method according to the invention is longitudinally flanked by two frustoconical portions each having its large diameter base turned away from said small diameter cylindrical portion. If desired, the base side of a frustoconical portion or of each frustoconical portion, as the case may be, of each sensor may merge into an outer cylindrical portion having the same diameter as the base.

In the performance of the method according to the invention it is possible to use any kind of glass fibres such as chalcogenic compound based glass fibres, silica glass fibres, fluoridic glass fibres and the like. The choice of the type of fibre depends, inter alia, on the range of the light spectrum at which measurements are performed.

The invention further provides for use in the performance of the above method a probe comprising a tubular casing adapted to hold a substrate medium and fitted within with at least one optical fibre sensor having an unclad sensing zone and a light incoming end, characterised in that the sensing zone of each sensor comprises a small diameter cylindrical portion merging at least on the side of the light intake end into a frustoconical portion whose large diameter base is turned away from said small diameter cylindrical portion.

In a preferred embodiment of the invention the small diameter cylindrical portion of the sensing zone of each sensor is longitudinally flanked by two frustoconical portions each having its large diameter base turned away from said small diameter cylindrical portion. If desired, in such an embodiment the base side of a frustoconical portion or of each frustoconical portion, as the case may be, of each sensor may merge into an outer cylindrical portion having the same diameter as the base.

The cylindrical casing of a probe according to the invention may have a circular or polygonal cross-sectional shape.

Due to the specific geometry of the sensor(s) in a probe according to the invention the sensitivity of the sensing zone of each sensor is significantly increased. This is due to three cumulative effects: For one, the frustoconical portion on the light intake side increases the incidence angle in the small diameter portion of the sensing zone of each sensor and by this the depth of penetration of the evanescent light wave into the test fluid is increased. Secondly, due to the small diameter of the sensing zone portion of each sensor, the number of internal light reflections per unit length is increased. Thirdly, the frustocopical portion on the light intake end side concentrates the incoming light. In consequence of these three effects there is an increased interaction between the evanescent light wave in the sensing zone of each sensor and the surrounding test medium whereby the sensitivity of the sensor(s) is significantly increased.

Due to the high sensitivity of the sensor(s) in probes according to the invention there is no need for any sensitizer reagent and the test fluid can be measured directly.

Where a probe according to the invention has two or more sensors they will be referred to hereinafter as "bundle".

In accordance with one embodiment of a sensor bundle in a probe according to the invention the sensing zones of all sensors remain discrete entities and each sensor operates independent of the other. In this way the sensitivity of the assembly is increased as compared to a single-sensor probe due to an increase of the contact area between the sensors of the test medium and thereby an increase of the effective volume of the test medium. Such probes are useful, for example, in the continuous monitoring of test fluids such as dilute solutions, emulsions and aerosols holding small amounts of test material per unit volume.

In accordance with another embodiment of a probe according to the invention having a sensor bundle the sensing zones of all sensors of the bundle are fused together into one single sensing zone while the light intake and light emitting end

portions and the frustoconical portions on both sides remain discrete entities.

In a particular form of such a probe each discrete intake end portion is associated with a discrete emitting end portion at the light transmitting end to form a couple and each such couple is designed to transmit light at a wavelength different from that transmitted by all other couples.

If desired, each of the discrete end portions of a sensor bundle in such a probe may be connected to a separate photoelectric detector of the photoconductive or photovoltaic type.

A probe in accordance with this embodiment is useful for simultaneous reading of the absorption of the test material at different wavelengths and in this way there is no need for any scanning of the test material by continuously changing the wavelengths as is required in conventional spectrometry, which is an obvious significant advantage. If desired, the discrete readings obtained in this way may be processed into an integrated continuous absorption curve.

Due to the high sensitivity of the probe according to the invention only small quantities of test medium are required for the performance of a conclusive spectral analysis. Accordingly, in accordance with one embodiment of the invention the probe has capillary dimensions which are determined by the effective volume of penetration of the evanescent wave in the sensing zone of the sensor or sensors, as the case may be. Due to the high sensitivity the sensors, in the probes according to the invention yield reliable results in real time.

A probe according to the invention may be designed for use in a batch mode of operation or for continuous use. In the batch mode the probe may serve for one-time use only and upon completion of the spectral analysis the probe with the contents may either be discarded or be stored as reference for future measurements. Due to the intrinsically small size of the probes according to the invention for use in the batch mode, these probes are readily transportable which enables to perform the sampling for the batch mode remote of the ATR instrument, which is yet another obvious advantage.

Alternatively, a probe according to the invention may be designed as a so-called dynamic probe adapted for a continuous mode of operation with constant throughflow of a test fluid. Such an embodiment is useful for continuous ATR monitoring.

The casing of the probe may be made of any suitable material. During storage the probe may, if desired, be filled with an inert liquid in order to protect in this way the unclad sensing zone of the sensor(s).

During filling, storage and transportation the probes according to the invention used in the batch mode are preferably capped.

For the preparation of an optical fibre sensor having the shape required for mounting in a probe according to the invention, an optical fibre core is first produced by drawing a preform in a drawing tower as known per se. Where the resulting optical fibre is immediately further processed there is no need for cladding. If, however, the further processing for imparting it the geometry required according to the invention is deferred, the fibre is preferably clad and the cladding is subsequently removed, e.g. by etching, prior to further processing.

For the manufacture of a probe according to the invention optical fibres are first processed for imparting them the geometry required in accordance with the invention. Such processing comprises cutting a stretch of optical fibre into pieces of desired lengths and putting each piece individually or alternatively a bundle of such pieces in a suitably designed heat-stretching device. In a preferred embodiment such heat-stretching device comprises two aligned holder tubes of which at least one serves as casing of the finished probe. The aligned holder tubes are spaced from each other to form a gap at which the fibre is exposed. The end portions of the fibres emerge at the far ends of the holder tubes and two equal weights are suspended therefrom. The exposed central region of the fibre or fibre bundle is then heated whereby it is softened and stretched in consequence of the pulling action of the two weights. In the course of such stretching conical portions are formed between the elongated, small diameter central cylindrical portion and the outer cylindrical portions having the original diameter. The device also has stops which arrest the weights when the fibre(s) has been stretched to the desired extent.

Upon completion of the above fibre shaping operation the fibre(s) is or are cut to size to yield the desired sensor(s), the two ends of each sensor are polished as known per se and the sensor(s) is or are shifted into that tubular holder that is to serve as casing of the probe and is or are properly centered and secured therein.

Where the sensor in a probe according to the invention is to have only one single conical portion the product of the above operation is cut in the central, small diameter portion and each half is shifted into one of the holder tubes and is then properly centered and secured therein.

For the production of a probe according to the invention with a bundle of fibres having a common, single sensing zone, the bundle is twisted during heating whereby the sensing zones are fused together. Such twisting may, for example, be effected by revolving the two holder tubes in opposite directions.

DESCRIPTION OF THE DRAWINGS

For better understanding the invention will now be described, by way of example only, with reference to the annexed drawings, it being understood that the invention is not restricted thereto. In the drawings:

Fig. 1 is an elevation of a sensor for use in a probe according to the invention also showing diagrammatically the increase of the number of reflections per length unit in the small diameter portion of the sensing zone;

Fig. 2 is an axial section of a probe according to the invention with a single sensor;

Fig. 3 is a cross-section along the line III-III of Fig. 2;

Fig. 4 is a cross-section of a probe according to the invention with a bundle of sensors;

Fig. 5 is a diagrammatic illustration of the production of an optical fibre sensor for a probe according to the invention;

Fig. 6 is a block diagram of an IR spectrometer operating by the ATR method in accordance with the invention;

Fig. 7 is an infrared absorption spectrum of paraffin in a probe with a single sensor according to the invention; and

Fig. 8 is an absorption spectrum of the paraffin using a prior art probe with a single sensor of Fig. 7 comprising however a single fibre shaped sensor according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

Fig. 1 shows an optical fibre sensor used in probes according to the invention. As shown the sensing zone of the sensor comprises a central cylindrical portion 1 of a small diameter D1 flanked by two conical portions 2 whose base 3 is turned away from the central portion 1 and each of which merges into another cylindrical portion 4 of larger diameter D2.

It should be noted here that Fig. 1 and also the following Figures are not drawn to scale and that actually D2/D1 is significantly larger than shown in the drawings.

In Fig. 1 the manner in which the conical portion 2 on the light intake side condenses light so as to increase the number of reflections per length unit is shown diagrammatically by means of notional light rays 5 and 6. It is clearly seen that the distance between the reflection points of these two rays at the fibre surface diminishes gradually from the large diameter cylindrical portion 3 via the conical portion 2 and is at its smallest within the small diameter cylindrical portion 1. In other words, in the small diameter cylindrical portion 1 the number of reflections per length unit is much larger than in the large diameter cylindrical portion 4.

In use all or part of the small diameter portion of the sensing zone of a shaped optical fibre sensor of the kind shown in Fig. 1, is in contact with a test medium and an evanescent lightwave propagates at the test medium/sensor interface. The intensity of the interaction between the evanescent light wave and the surrounding medium is directly proportional to the diameter ratio D2/D1 and to the length L of the small diameter portion 1. The ratio of diameters is, however, limited by the requirement that the resulting incidence angle must remain below the critical angle so that the light in the fibre remains within the precinct of total reflection. The critical angle increases with the difference between the refraction indices of the sensor and test medium and consequently sensors with a high refraction index are, as a rule, preferred, e.g. such as are made of chalcogenic glass. Subject to the above limitation, it is desirable to design a sensor in a probe according to the invention in such a way that the central portion 1 is as thin and as long as practically possible.

A typical example of a probe according to the invention for use in the batch mode of operation and having a single fibre sensor is illustrated in Figs. 2 and 3. As shown a probe 7 comprises a tubular casing 8 of circular cross-sectional shape. Casing 8 comprises two sealable openings 9 for the introduction of a sample medium.

An optical fibre probe 10 is held within two annular bodies 11 having a tapering cross-sectioned shape and made of light blocking material. The shape of the sensor 10 is similar to that shown in Fig. 1 and it comprises a small-diameter central cylindrical portion 12 longitudinally flanked by two conical portions 13 merging each into a second, large diameter cylindrical portion 14. The ends of portion 14 are suitably polished as known per se and during filling, storage and transportation they are protected by means of caps 15.

A probe according to the invention for use in the continuous mode of operation is in principle of similar design with the openings 9, however, being preferably replaced by inlet and outlet tubes.

The probe according to the invention shown in cross-section in Fig. 4 is essentially similar to that of Figs. 2 and 3 with the single fibre sensor being however replaced here by a bundle of sensors, similar components being designated the same numerals. As shown, the single fibre sensor 10 of Figs. 2 and 3 is here replaced by a bundle 16 comprising a plurality of individual fibres 18 each having a central small diameter portion 19 longitudinally flanked by two conical portions 20 (only one being shown in Fig. 4) and each merging into a large diameter cylindrical portion (not shown).

In the embodiment of Fig. 4 all sensors of the bundle 16 remain as discrete entities. Alternatively, a bundle may be used with a single sensing zone and discrete frustoconical and end portions.

The preparation of a probe with an optical fibre sensor according to the present invention is illustrated diagrammatically in Fig. 5. As shown, an optical fibre piece 22 of suitable length and diameter (50 - 1000 μ) is enclosed within two aligned capillary holder tubes 23 separated by a gap 24. At the two ends of the optical fibre 22 there are attached strings 25 each of which is supported by a pulley 26 and from each of which there is suspended a weight 27, the two weights 27 being exactly equal.

Underneath weights 27 there are provides stops 28 which are removed from the initial positions of the weights by a distance L/2 where L is the length of the sensing zone in the finished sensor.

The exposed portion of fibre 23 stretching across gap 25 is heated whereupon that portion softens and stretches with a concomitant reduction of its diameter and the formation of transitional conical portions between the stretched, small diameter central cylindrical portion and the flanking unstretched, large diameter cylindrical portions of fibre 25. This stretching operation continues until weights 27 are arrested by stops 28 whereupon the heating is interrupted. The product shaped fibre is then cut to size and shifted into one of the holder tubes 23 that serves as casing in the finished probe according to the invention. The ends of the sensor may then be polished as known per se and finally the sensor is centred and recessed in any suitable manner as known per se.

When a sensor with only one conical portion is required the product shaped fibre is cut at the small diameter central portion and each resulting sensor is shifted into one of tubes 23 which is then followed by the same operations as mentioned above.

The preparation of a probe with a bundle of discrete sensors is essentially similar.

For the preparation of a probe comprising a sensor bundle with a single sensing zone spreading at both ends into a plurality of discrete frustoconical and end portions, a bundle of discrete fibres is used and the stretching operation is combined with a twisting operation, e.g. by revolving the two holder tube 23 in opposite directions, whereby the exposed portions of all fibres 22 of a bundle are fused together with simultaneous stretching.

Fig. 6 is a block diagram of one embodiment of an ATR assembly for recording an IR spectrum with the use of a probe according to the invention. As shown, the spectrometer assembly comprises a light source 30, a splitting mirror 31, a sample probe 32, a reference probe 33, end detectors 34 and 35 and an analyser 36. In operation IR light emanating from light source 30 is split by splitting mirror 31 whereby two rays are created, one which passes through sample probe 32 and the other which passes through reference probe 33. End detectors 34 and 35 detect the modulations of the evanescent light emanating from the sample probe 32 and the reference probe 33 respectively and the analyser 36 compares the signals produced by the detectors to give a qualitative spectrum and/or an indication of sample concentration.

Instead of employing a splitting mirror 31 it is also possible to connect the sensors of each of the sample probe 32 and reference probe 33 directly to the light source 30.

A COMPARATIVE EXAMPLE

In a first experiment the IR spectrum of a single paraffin drop measuring 0.2 mm was recorded, using a probe according to the invention having a single optical fibre sensor made of As_2Se_3 chalcogenic glass and having a refractive index of 2.77. The configuration of the sensor was similar to that shown in Fig. 1 with the sensing zone being 2 cm long and having a diameter of 20 μ while the diameter of the flanking cylindrical portions was 500 μ. The paraffin drop was thus in contact with a small portion of the sensing zone.

In a second experiment a large size conventional probe was used with a single optical fibre sensor of the same chalcogenic glass, 500 μ diameter and having a sensing zone of 20 cm length. The quantity of paraffin in the second experiment was much larger so as to surround the entire length of the optical fibre sensor. In both experiments a Nicolet FTIR spectrometer was used with a reflective optical system for concentrating the light on the sensor. The light emerging from the sensor was measured by external MCT detector that was directly connected to the analyser. Fig. 7 shows a tracing of an SR spectrum recorded in the first experiment and Fig. 8 shows a tracing of an IR spectrum recorded in the second experiment. By comparing these two tracings it is evident that the sensitivity and resolution power achieved in accordance with the invention is significantly higher than those achieved with a prior art probe. In fact, when comparing the lengths of the contact area of the sensing zone in the experiment with the probe according to the invention which was 0.2 mm, with the length of the contact area in the experiment with the conventional probe which was equal to the length of the probe, i.e. 20 cm (in that experiment the entire sensor was in contact with the paraffin), it

can be shown that the sensitivity of a probe according to the invention is about 2000 fold of that of a conventional optical fibre probe.

Claims

1. A method of performing a spectroscopic measurement by the attenuated total reflection (ATR) technique employing a tubular probe adapted to hold a substrate medium and fitted within with at least one optical fibre sensor having an unclad sensing zone and light intake and emitting ends, characterised in that the sensing zone of each sensor is a small diameter cylindrical portion merging at least on the side of the light intake end into a frustoconical portion whose large diameter base is turned away from said small diameter cylindrical portion.
2. A method according to claim 1, characterised by using a probe in which the small diameter cylindrical portion of the sensing zone of each sensor of the probe is longitudinally flanked by two frustoconical portions each having its large diameter base turned away from said small diameter cylindrical portion.
3. A method according to claim 2, characterised by using a probe in which the large diameter base side of each frustoconical portion of each sensor merges into an outer cylindrical portion having the same diameter of said base.
4. A method according to any one,of claims 1 to 3, characterised by using a probe having a single sensor.
5. A method according to any one of claims 1 to 3, characterised by using a probe with a bundle of discrete sensors.
6. A method according to claim 5, characterised by using a probe with a bundle of sensors in which all sensing zones are fused together while the frustoconical portions and the intake and emitting end portions remain discrete entities.
7. A method according to claim 6, characterised in that in said bundle each discrete intake end portion is associated with a discrete emitting end portion to form a couple and each such couple is designed to transmit light at a wavelength different from that transmitted by all other couples.
8. A method according to claim 7, characterised in that each of the discrete emitting end portions of the bundle is connected to a separate photoelectric detector.
9. A method according to claim 8 characterised in that simultaneous readings of the light emitted from each discrete emitting end portion is processed into an integrated absorption curve.
10. A method according to any one of claims 1 to 9 for the performance of spectroscopic measurements with light in any one of the ultraviolet, visible and near infrared regions, characterised in that a probe is used in which each sensor is made of silica or fluoride based glass fibre.
11. A method according to any one of claims 1 to 9 for the performance of spectroscopic measurements with light in the far infrared region, characterised in that a probe is used in which each sensor is made of a chalcogenic compound based glass fibre.
12. For use in the performance of a method according to any one of claims 1 to 11, a probe comprising a tubular casing adapted to hold a substrate medium and fitted within with at least one optical fibre sensor having an unclad sensing zone and light intake and emitting ends, characterised in that the unclad sensing zone of each sensor is a small diameter cylindrical portion merging at least on the side of the light intake end into a frustoconical portion whose large diameter base is turned away from said small diameter cylindrical portion.
13. A probe according to claim 12, characterised in that the small diameter cylindrical portion of the sensing zone of each sensor is longitudinally flanked by two frustoconical portions each having its large diameter base turned away from said small diameter cylindrical portion.
14. A probe according to claim 12 or 13, characterised in that the large diameter base side of each frustoconical portion of each sensor merges into an outer cylindrical portion having the same diameter as said base.
15. A probe according to any one of claims 12 to 14, characterised in that the cylindrical casing has a circular cross-sectional shape.
16. A probe according to any one of claims 12 to 14, characterised in that the cylindrical casing has a polygonal cross-sectional shape.
17. A probe according to any one of claims 12 to 16, characterised by comprising a single sensor.
18. A probe according to any one of claims 12 to 16, characterised by comprising a bundle of discrete sensors.
19. A probe according to any one of claims 12 to 16 characterised by comprising a bundle of sensors in which all sensing zones are fused together while the frustoconical portions and the intake and emitting end portions remain discrete entities.
20. A probe according to claim 19, characterised in that each discrete end intake end portion is associated with a discrete emitting end portion to form a couple and each such couple is designed to transmit light at a wavelength different from that transmitted by all other couples.
21. A probe according to any one of claims 12 to 20, characterised by each sensor being made of silica or fluoride based glass fibre.
22. A probe according to any one of claims 12 to

21, characterised by each sensor being made of chalcogenic compound based glass fibre.

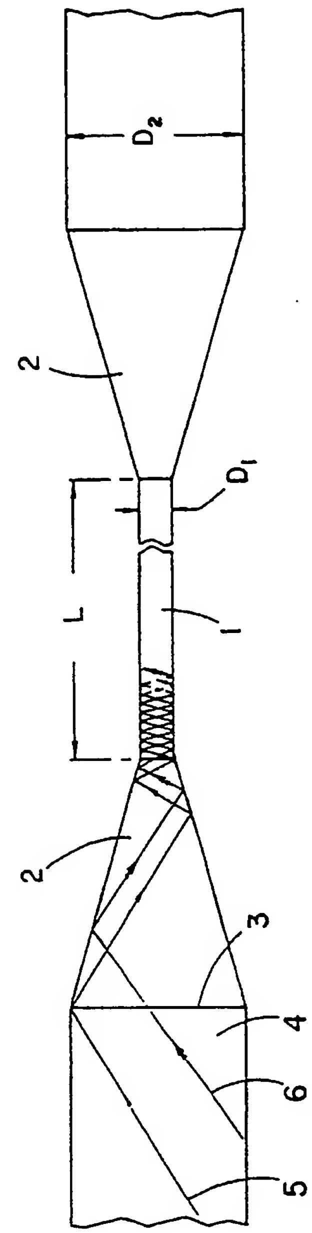

Fig. 1

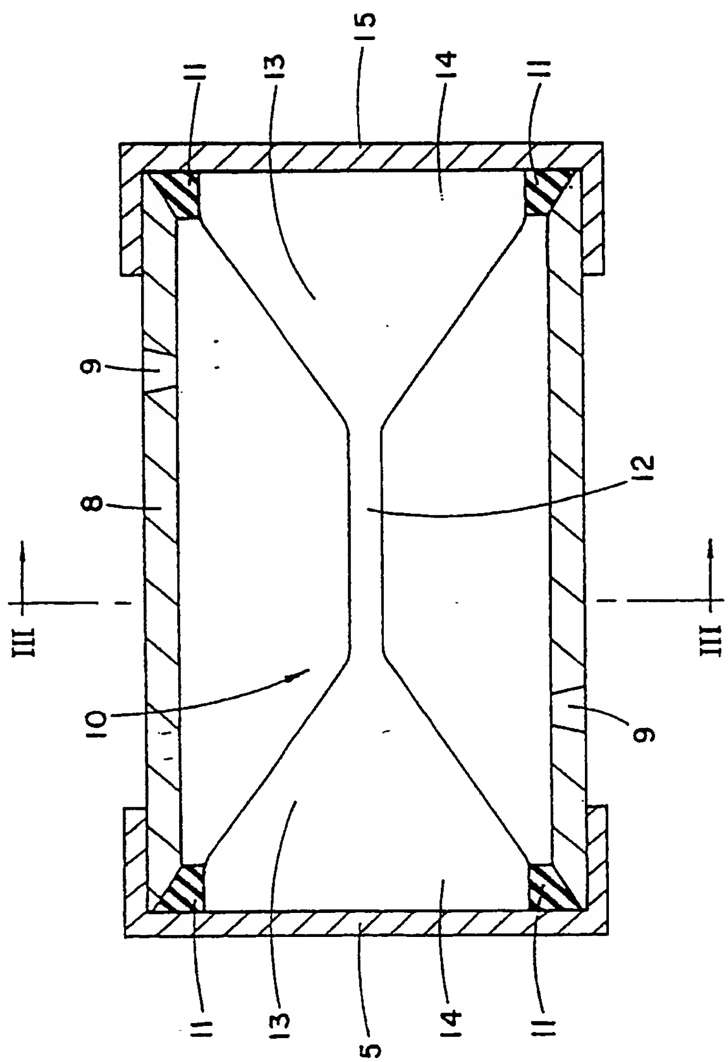

Fig. 2

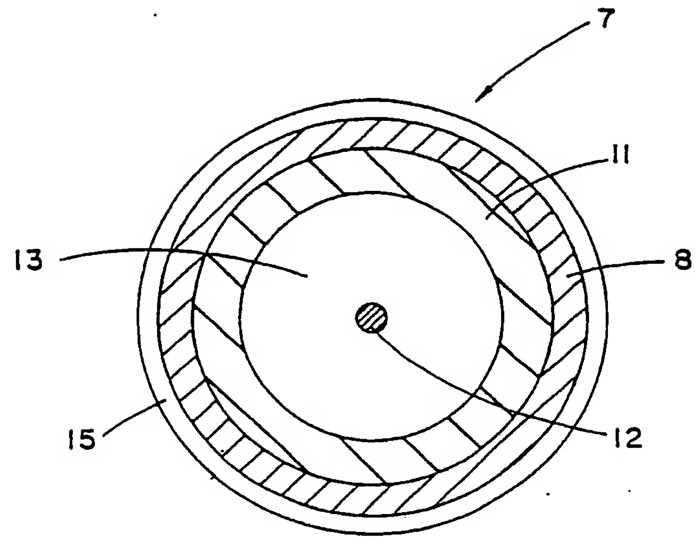

Fig. 3

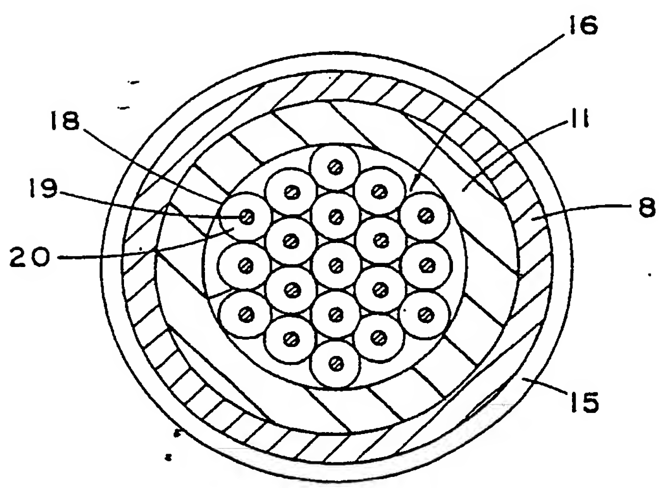

Fig. 4

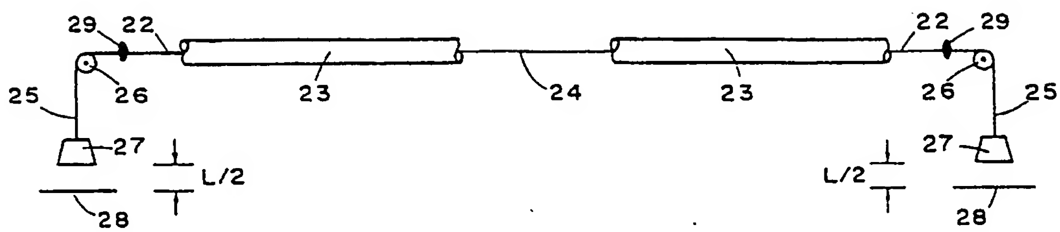
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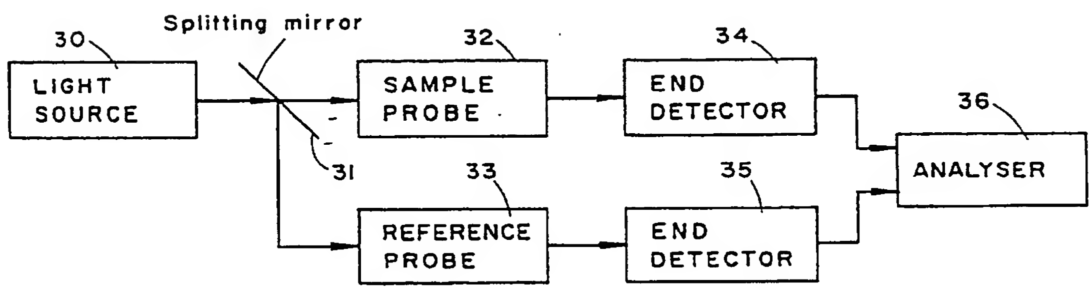
Fig.5


Splitting mirror
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LIGHT SOURCE
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SAMPLE PROBE
33
REFERENCE PROBE
34
END DETECTOR
35
END DETECTOR
36
ANALYSER

Fig.6

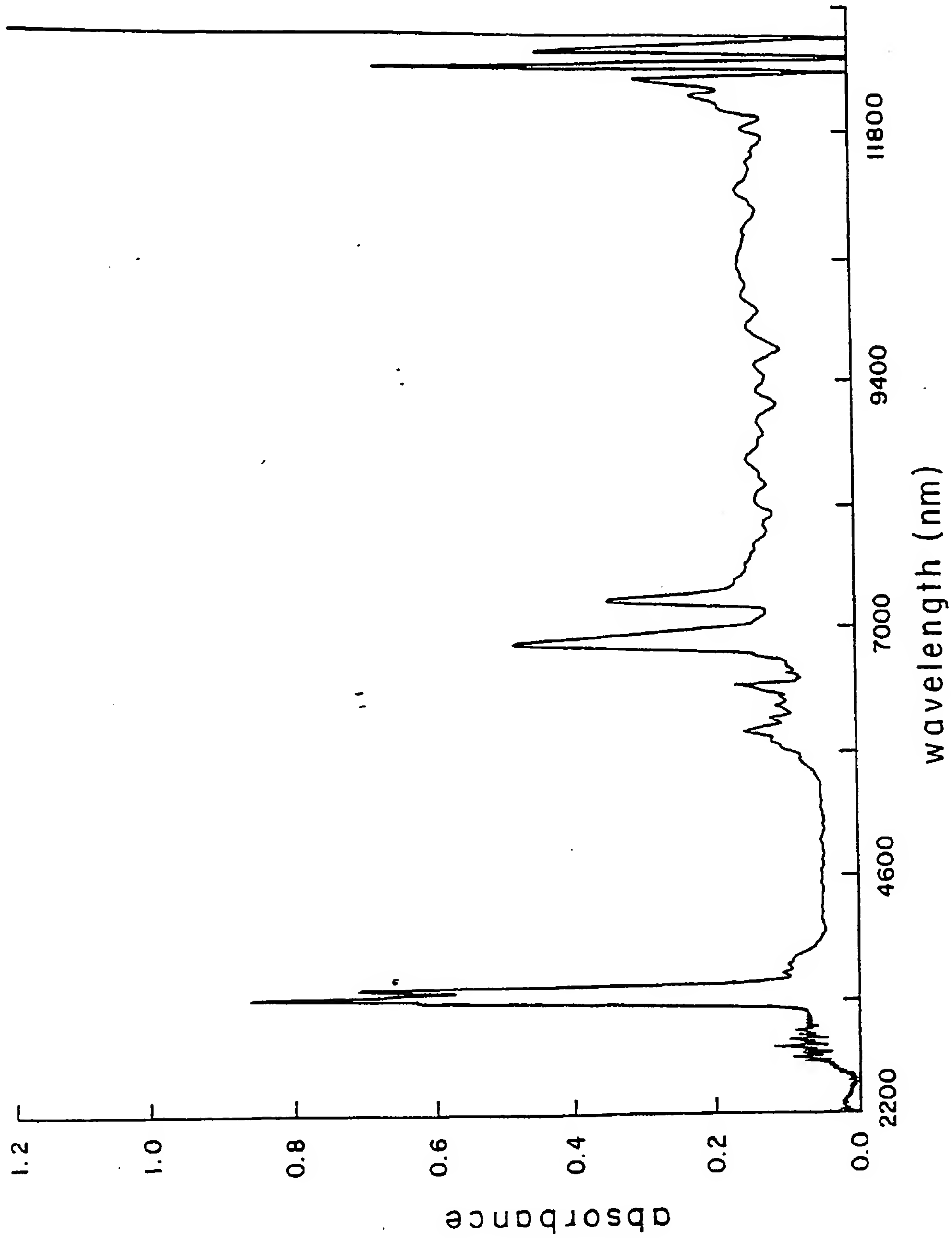

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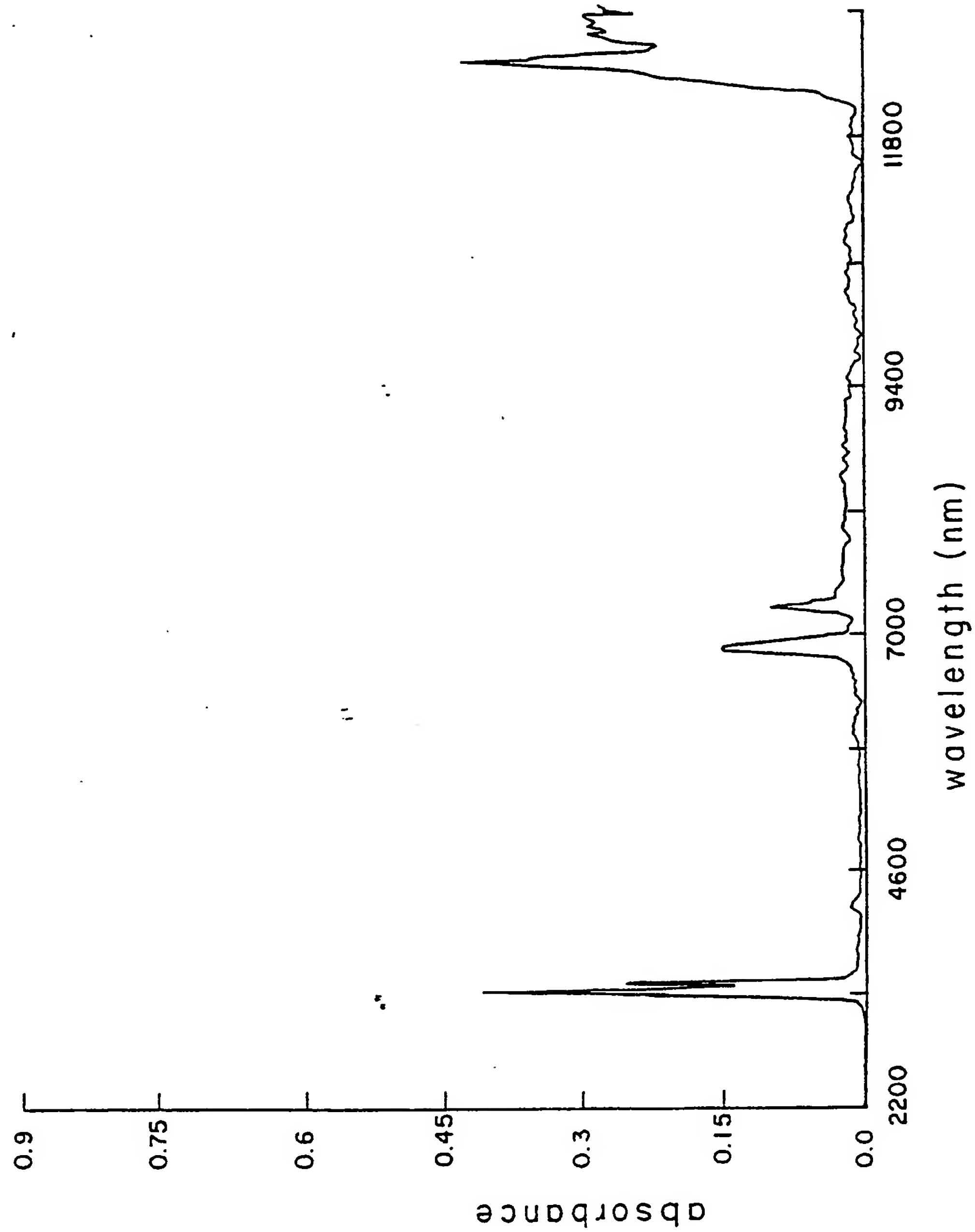
Fig. 7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wavelength (nm)

Fig. 8